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Electrical phenomena observed upon rapid separation of mercury from interfacial contact with methylmethacrylate polymer

Palmer, Philip Maynard

Ohio State University

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ELECTRICAL PHENOMENA OBSERVED UPON RAPID SEPARATION OF MERCURY FROM INTERFACIAL CONTACT WITH METHYLMETHACRYLATE POLYMER

PHILIP MAYNARD PALMER

ELECTRICAL PHENOMENA OBSERVED UPON RAPID SEPARATION OF MERCURY FROM INTERFACIAL CONTACT WITH METHYLMETHACRYLATE POLYMER

A Thesis

Presented in Partial Fulfillment of the Requirements
for the Degree Master of Science

by

Philip Maynard Palmer, B.S.

* * * * * * *

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Approved by

_____
Adviser
Department of Chemistry

ACKNOWLEDGMENT

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INTRODUCTION

The original intent of this research was to attempt a correlative study of the data offered by Deryagin (4) and Skinner (13) by applying the experimental technique proposed by Deryagin to modifications of the systems reported by Skinner, thus verifying the findings of Skinner by a more rigorous experimental method.

During the course of experimentation it was discovered that the electrical data which was obtained possessed a certain time dependence which might possibly yield information concerning the mobility of the charge carriers producing the observed electrical phenomena and their distribution within the bulk of the polymer film. It was along these lines that research subsequently proceeded.

REVIEW OF LITERATURE

Electrical phenomena including atmospheric arcing, after-emission from the detached surfaces, electrostatic clinging of detached surfaces and electron flow through connected external electrical circuits have been noted by many observers (4), (10), (12), (13), (15), (16) during and after the rapid separation of solid-solid and solid-liquid interfaces. These phenomena have been the subject of considerable philosophical discussion and debate. Arguments have been offered to support not only the theory that electrical forces contribute significantly to the adhesion forces at these interfaces (13) but also to support the theory that electrical forces can contribute little to the total adhesion forces (6), (16). Some authors have merely stated that these electrical phenomena provide no information at all concerning the nature of interfacial adhesion forces but are merely a mechanical effect (11). Unfortunately, little research has been done to provide quantitative proof to support any of these contentions. Because of the paucity of experimental work which has been carried out to date, it will be possible to review rather completely here what work has been done.

Among the earlier works in the field is that of Skinner who has worked primarily with the systems of copper or aluminum bonded by polymethylmethacrylate films. Two of his experiments and the conclusions he drew from them are of interest here: 1) the measurement of residual electrostatic charge existing on the surfaces of metal buttons bonded together by polymer film after failure under tension by means of a Faraday pail, and 2) the effect of an applied D. C. voltage on the stress-strain behavior of the polymer film. The more important conclusions of this investigator are:

1) there is a measurable charge transfer in an external

electrical circuit upon sudden rupture of the sample of

the order of 10^8 to 10^{13} electrons per square centimeter,

2) the charge transferred is a function of the nature of

metal surface and adhesive,

3) the electrostatic component of adhesion is a linear

function of the breaking strength of adhesive,

4) the actual charge distribution in the adhesive includes

a volume distribution which shows a large decrease when

large transfer occurs being essentially complete within

10^{-7} centimeters,

5) stress-strain curves can be appreciably altered by

application of a potential across the polymer film, and

6) charge density at the interface is not a function of

film thickness.

Russian investigators comprise the large majority of writers

who favor the theory that electrical forces play a large role in inter-

facial adhesion. Prominent among these are Deryagin, Krotova

and Voyutskii.

Krotova (10) has worked primarily with polymer-polymer

systems and has been concerned chiefly with charge transfer resul-

ting from donor-acceptor interactions between adhesive and sub-

strate. Using luminescence methods on thin cross-sections of con-

tacting solid polymers, she established that the extent of interaction

was a function of time of contact, temperature of contact, surface

history and the nature of the functional groups of the two polymers.

IR spectroscopy studies of the surfaces after cleavage of adhesive

from substrate established the existence of donor-acceptor interactions

between the functional groups of the polymer pair. Using an electro-

meter to measure charge transfer during failure of the bond, a

Faraday pail to measure residual charge and a multiplier-oscillator

circuit to measure after-emission intensities, she also showed that

the ability of various adhesive functional groups to impart electro-

static charge to a substrate corresponded to the positions of the

functional groups in the donor-acceptor series. This latter finding

is in agreement with a study made recently by Lewis and Forrestal (11) in which they concluded that electron acceptor functional groups are the best enhancers of polymer adhesion to metal substrates.

Deryagin developed a method for directly measuring the electrical double layer charge density at a metal-polymer interface. He reasoned that, in the case of very thin films, it was possible to perform rapid separation of the interface without producing atmospheric discharge, a problem Skinner had not been able to overcome and which, therefore, cast uncertainty into his results. To facilitate the separation process and improve reproducibility he further suggested that mercury be used as one of the metals in the system. Utilizing systems of steel - SKN40 - mercury and steel - cellulose - mercury, he measured charge transfer by means of a ballistic galvanometer as a function of film thicknesses ranging from 0.1 to 10 μ. The highest charge measured was of the order of 10^{-7} coulombs per square centimeter. He concluded as a result of his experiments that: 1) there is a definite separation of charge at a metal-polymer interface and 2) the density of the electrical double layer is a function of the film thickness and increases sharply as film thicknesses become very thin. The latter conclusion seems to be in direct opposition to the conclusion of Skinner until one recalls that Skinner was talking about thicknesses well in excess of 10^{-7} centimeters whereas Deryagin is dealing in extremely small

thickness ranges. A very complete mathematical treatment of this theory is given by Deryagin in reference (5).

The question yet to be answered at which this research was directed is the specification of the exact mechanism which operates at these solid-solid and solid-liquid interfaces to produce the observed electrical phenomena and to relate this to adhesive forces existing at the interfaces. An excellent work which reviews current research and thinking on this question has been written by Voyutskii (16). Most writers agree in the case of metal-polymer systems that the operating mechanism which first produces adhesion may be stated in general terms as one of adsorption. However, adsorption is usually thought of in terms of van der Waals inter-actions and hydrogen bonding. These forces can account for bonding strengths of up to 500 calories per mole but actual bond strengths have been measured as high as a thousand times that amount (16). Therefore, it seems apparent that other forces must be at work in the metal-polymer systems. The data of Skinner and Deryagin tend to support the view that a type of direct electron transfer occurs between the two phases. Skinner suggests that an electron atmos-phere exists within the polymer with electrons available at discrete energy levels within the polymer and that a Fermi level equilibrium is established between metal and polymer. But since Deryagin has demonstrated the existence of a bulk charge distribution within the

polymer, this picture of Skinner is much too simple. Further, polymethylmethacrylate used by Skinner as his polymer is an insulator in that the ϕ-x gap is too large to allow ordinary electron transfer to occur. Vick (15) suggests two mechanisms by which it would be possible for direct electron transfer to occur: 1) the Fermi level, ϕ, of the metal might be reduced by electropositive adsorption on its surface, thus reducing ϕ-x and 2) surface sites on the insulator might exist which are electron acceptors or donors as a result of impurities in the polymer or the presence of functional groups in the polymer. It seems to this author that a third possibility exists, that of defects in an electronegative adsorbed film on the metal surface such as an oxide layer which provides local sites for electron transfer.

In summary it may be said that the literature concerning the interfacial conditions existing in solid-solid and solid-liquid contact is given at present to a rather sparse but lively dialogue offering various divergent opinions relative to the forces which contribute to adhesion between two phases. Experimental work in these systems is almost non-existent and the validity of the work by the Russian group in examining electrostatic phenomena at these interfaces is severely questioned by many scientists. If this work were to be invalidated, the remaining experimental literature would be almost nil. In short, at the present time the state of knowledge of the

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adhesive nature of solid-solid and solid-liquid interfaces remains very much an art rather than a science. The literature provides much information on how to prepare specific adhesives for specific systems but there is no general theory or set of theories to allow one to predict the structure or nature of an adhesive which would be best for a general type of adhesive system or the magnitude of adhesive strength which would result in such a system.

EXPERIMENTAL

Materials

All chemicals used were analytical grade reagents. Glass-
ware was used for transporting and storing mercury to avoid
contamination except for elbow connections where rubber vacuum
tubing was utilized of necessity. High purity copper rod was used in
the fabrication of the copper test plugs.

Apparatus

The test cell was fabricated from 1/4 inch lucite and is illus-
trated in Figure 1-a. It was designed to provide a vacuum tight
chamber ahead of the test plug face with the plug collar greased with
stop cock grease to provide a vacuum seal between plug and cell.
The test plugs were machined from copper rod stock on a lathe and
are shown in Figure 1-b. Charge transfer was measured by means
of a Leeds and Northrup Ballistic Galvanometer, Model Number 2239
having a scale sensitivity of 0.0018 micro coulombs per millimeter
at one meters distance when used with the recommended lamp and
scale reading device. The galvanometer period was 26.8 seconds.
Vacuum was provided for pulling mercury from the reservoir into

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the test cell by means of a standard laboratory model oil vacuum pump. The complete apparatus layout is shown in Figure 2.

For measurements on the mercury-polymer-mercury system a blank plug was also fabricated for use in the same apparatus set up just described. The plug was fabricated from block Lucite on a lathe and is pictured in Figure 1-c.

In order to measure the influence of electrical field on interfacial phenomena, a source of EMF was constructed which provided potentials from 0 - 502 volts in approximately 62 volt increments when connected across an insulator such as the polymer film. Thus, field intensities were achieved from 0 - 65,000 volts per centimeter.

A Faraday pail was made for use in experiments where a Lucite rod was withdrawn from mercury instead of withdrawing mercury from the polymer surface. The Faraday pail is shown in Figure 3.

Procedures

The copper plugs were degreased by immersion in an ultrasonic bath for fifteen minutes using a Brownwill Biosonik transducer as the emission source and benzene as the solvent. The plugs were then polished using 0000 polishing emery paper followed by a dilute slurry of Beuhler AB Gamma polishing alumina, number 3 on an eight inch metallurgical polishing wheel. The plugs were then washed under a moderate stream of distilled water and dried in a

vacuum dessicator. On subsequent runs after the initial polymer application it was not necessary to repeat the polishing step but the degreasing procedure was repeated after each run in order to remove the polymer film from the previous run prior to reapplication.

Adhesive was prepared for application to the copper test plugs from Rohm and Haas methylmethacrylate monomer which contained an inhibitor. The inhibitor was removed by washing 25cc portions of the monomer with 5cc of 5% NaOH (aq). The monomer was then rinsed twice with equal volumes of distilled water and the entrained water was subsequently removed by crystallization in a dry ice bath and filtering out the ice crystals on glass wool in a dry ice packed funnel. Next, ten milligrams of benzoyl peroxide were added to the monomer as a polymerization catalyst in small glass vials and the vials containing the monomer were placed in an oven at 70°C. for a period of three hours and twenty minutes. This time and temperature corresponds to 60% prepolymerization (13) at which stage the liquid prepolymer is noticeably viscous but still flows quite readily. If too much catalyst has been used, the prepolymer will be quite thick at this point and will have a strong tendency to entrain air bubbles when applied to the surface of the copper plug face. This must be scrupulously avoided since it not only introduces areas where contact between polymer and metal is absent but also allows paths along which mercury can penetrate to the copper surface

during testing, thus destroying the electrical integrity of the film.

The prepolymer was applied to the copper plug face by means of an eyedropper and spread over the surface with a porcelain spatula. The samples were placed on a board, face up, and then in the oven at 70°C. for the desired curing period. At the end of the curing period they were removed from the oven, cooled and then stored in a dessicator to await testing. Attempts to apply very thin films by pressing the plugs between Teflon covered boards were unsuccessful because the polymer could not be prevented from adhering to the Teflon surface. Drying the polymer out of a volatile solvent on the plug faces to obtain thin films was not used because of a desire to eliminate solvent effects from the experimental variables. As a consequence, film thicknesses of the order of 0.003 inches resulted. It was necessary to accept these thicknesses in order to achieve electrical integrity of the film across the entire plug surface, a condition absolutely essential to the success of the experimental measurements.

In taking measurements on the mercury-polymer-mercury system the blank plug was used in the test cell in place of the copper test plugs. The plug face in the blank plug was 0.030 inches thick.

The test cell was prepared for testing by first greasing the collar of the plug to be tested with high vacuum stop cock grease being sure not to get any grease on the surface of the plug face.

The plug was then set in place on the yoke in the test cell and carefully inserted through the window and clamped securely in place by means of the set screw on the back plate which also served as electrical contact for surface charge measurements. Next the mercury was raised into the test cell under vacuum and by means of a Simpson meter the integrity of the film was checked to assure that there were no electrical leaks between mercury and copper. Electrical connection was then made with the galvanometer as shown in Figure 2. The galvanometer had been previously calibrated with a known potential source and capacitor so that the name plate data could be confirmed and so that the electrical sign convention of Figure 4-a could be assigned. Finally, readings were taken by dropping the mercury from the cell into the reservoir and noting the galvanometer deflection. Mercury withdrawal velocity could be varied by changing the static head and/or the back pressure against which it was withdrawn through appropriate manipulation of the vacuum-air control valves.

For the experiments involving application of an external potential across the polymer film, the EMF was applied in the manner illustrated in Figure 4-b. The convention of Figure 4-a was used so that application of a positive EMF implies that during a static discharge of the polymer, a positive flow of current occurs as stated by the convention. Both static and dynamic readings were taken.

During static tests the system was charged by an external EMF and then discharged through the galvanometer. During dynamic tests the system was charged by an external EMF and then discharged through the galvanometer while at the same time withdrawing mercury from the cell. Since the period of the galvanometer was 26.8 seconds, all the charge transfer resulting from both discharge and from mercury withdrawal was incorporated in a single measured deflection and both effects could be observed simultaneously.

The Faraday pail measurements were made to check against external electrostatic influences in the test cell measurements. The lucite rod was cleaned, static charge removed in a stream of water and air dried prior to insertion in the mercury well. The rod was then removed from the well and the resultant charge residing in the mercury was measured by means of the galvanometer. Runs were made in sets which involved allowing surface film to accumulate on the rod between runs and in sets which involved cleaning the rod between each of the runs.
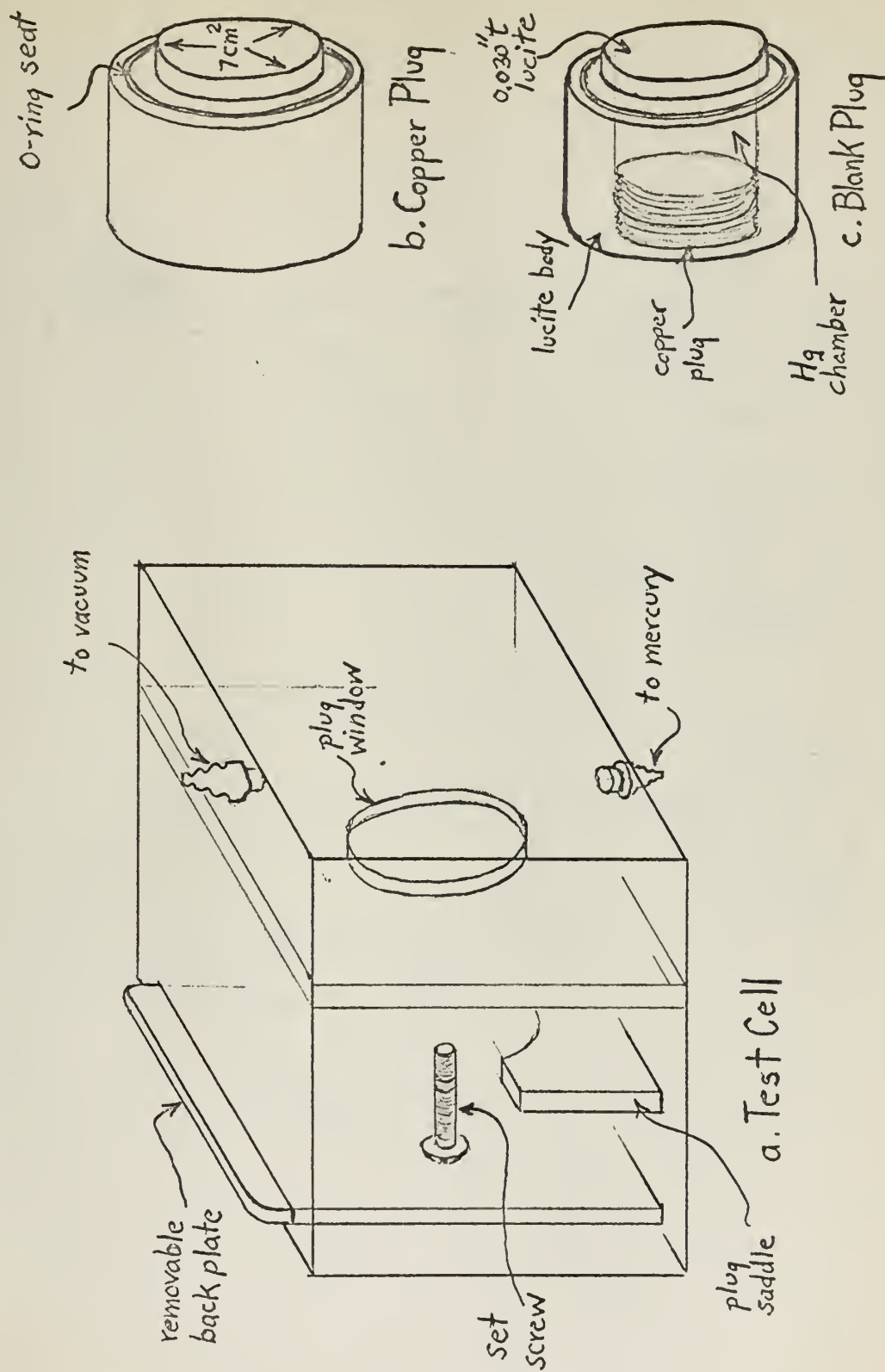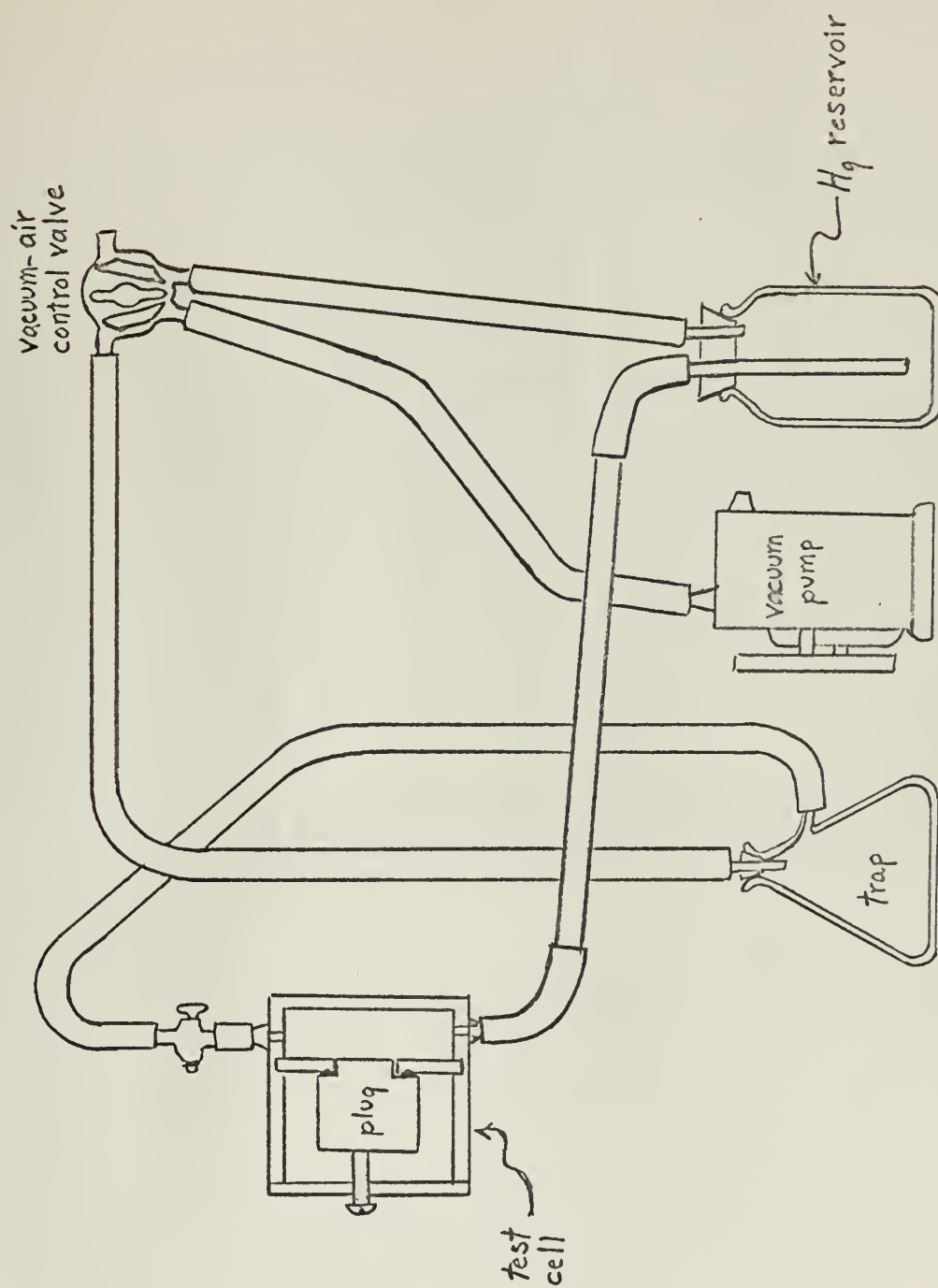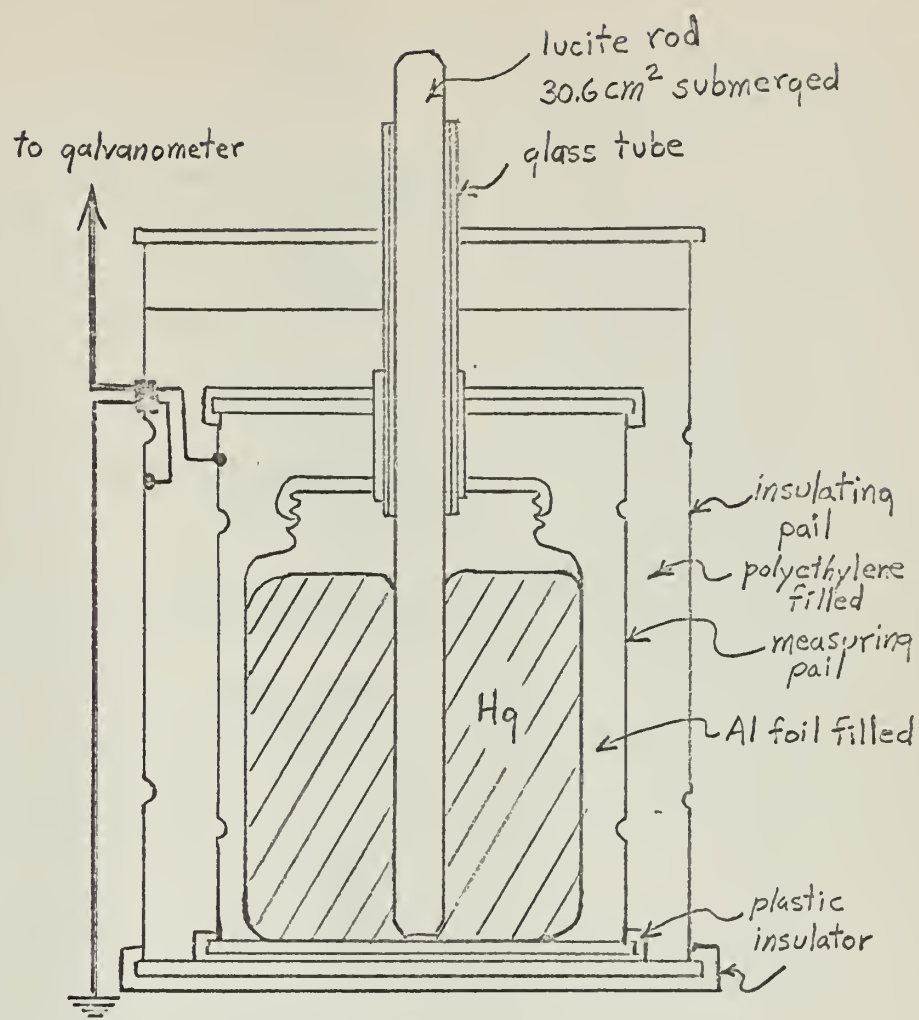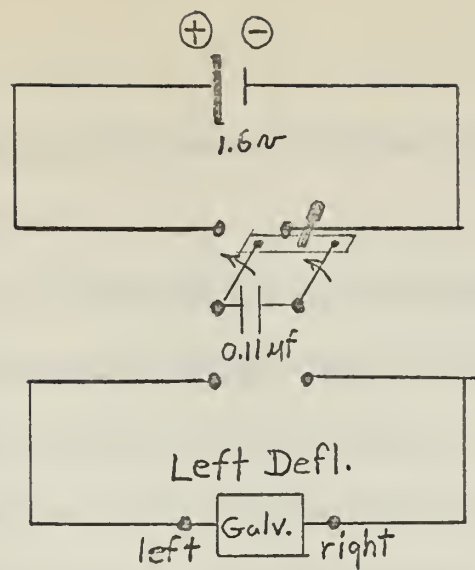
O-ring seat

7 cm²

b. Copper Plug

0.030"t lucite

c. Blank Plug

lucite body

copper plug

Hg chamber

to vacuum

plug window

to mercury

a. Test Cell

set screw

plug saddle

removable back plate

Figure 1.

Apparatus Layout
Figure 2.

lucite rod
30.6 cm² submerged

glass tube

to galvanometer

insulating pail

polyethylene filled

measuring pail

Al foil filled

Hg

plastic insulator

Faraday Pail
Figure 3.

a. Electrical Sign Convention.
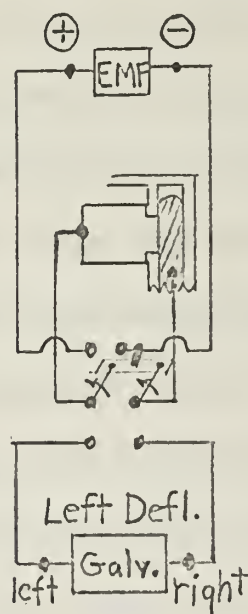
b. Wiring Arrangement for
Application of External Potential

Figure 4.

Results

The results of the experimentation are presented in Figures 5 through 9.

In Figure 5, the data are plotted for experiments performed using the adhesion test cell described by Deryagin. These data are for the copper-polymer-mercury system. Mercury was pulled across the polymer-coated copper plug face at a velocity of ten centimeters per second. Film thicknesses ranged between 0.002 and 0.003 inches for the samples tested. The observed galvanometer deflections converted to coulombs per square centimeter of plug face area are plotted for various lengths of curing time at 70°C. The different plotting symbols represent the several plugs on which runs were made. The data of Skinner showing the influence of cure time on total bond strength for copper plugs bonded together by polymethylmethacrylate are also plotted on this graph. It will be observed that both curves exhibit a maximum at a cure time of about fifteen hours. During the course of experimentation it was found that polymer films on plugs which were stored under normal room conditions (70°F., 65% relative humidity) remained solidly adherent whereas when the plugs were stored in a dessicator, a tendency toward detachment was observed after a period of over forty-eight hours after curing.

Figure 6 is a plot similar to that of Figure 5, except that, in these runs, the blank plug was substituted for the copper plug so that here we have two mercury phases separated by a polymethylmethacrylate film (actually a 0.03 inch Lucite sheet). In this set of experiments the times plotted along the abscissa represent the total lengths of time during which the mercury in the cell contacted the plug face prior to separation. The mercury within the plug, on the other hand, was in continuous contact with the inner plug face. Here again a maximum is exhibited but, in this case, it occurs after only fifteen minutes and at a value of charge transfer almost twice the magnitude of that for the copper plug experiments. During the runs a slow buildup of a black film was observed on the plug face which appeared to be a thin film of oxide. This film had not been observed in the case of the copper plugs where the polymer surface seemed much smoother.

The results of the Faraday pail experiments are given in Figure 7. Two curves are plotted. In both curves charge transfer in coulombs per square centimeter of contacting rod area is plotted against total contact time between rod and mercury. The data for one curve were taken under conditions where the rod was cleaned of surface film between runs. In the other curve surface film was allowed to accumulate between runs. It was noted that, if the rod was not cleaned between runs, a film resembling a thin mercury

coating appeared in patches on the surface so that at the end of about an hour the rod gave the appearance of being entirely coated in a thin layer of mercury. Under the mercury film the rod had acquired a light black film similar to that observed in the case of the blank plug.

Figure 8 represents the results of experimentation on the effect of mercury withdrawal rate on observed charge transfer. Charge transfer is plotted against the reciprocal of mercury withdrawal rate as measured by the rate of fall of mercury level within the test cell during evacuation. Rate of evacuation was varied by selective arrangement of the air-vacuum stop cocks to vary the head against which gravitational fall of mercury occurred and also by varying the height of the mercury column. Velocities ranging from 2 cm/sec to 10 cm/sec were obtained. The plot is linear and may easily be extrapolated to zero or what corresponds to instantaneous withdrawal of mercury from the cell.

The experiments in which the influence of electric field intensity on charge transfer was measured are summarized in Figure 9. Charge transfer is reported as before and electric field intensity is given in units of volts per centimeter. Experiments were performed on both the copper-polymer-mercury and the mercury-polymer-mercury systems. For each system both the static and dynamic curves are plotted. Thus, a total of four curves

are presented in the figure. Since the blank plug face was ten times

the thickness of the polymer film on the copper plugs, it should be

noted that the electric field intensity scales for the plots of the two

systems vary by a factor of ten. In reporting the results it was

necessary to adopt a sign convention and, for that purpose, the

scheme of Figure 4 was used. In this scheme, the deflection of the

galvanometer was observed for withdrawal of mercury with zero

potential applied to the system. This was then designated as positive

charge transfer. Next, the polarity of the potential which produced

a positive deflection when applied and discharged under static condi-

tions was observed. This was designated as the arrangement for

application of positive potential. Data is reported according to this

convention for both static and dynamic conditions. In the static

condition the mercury was held in the test cell while applying the

potential across the film and then discharging the system as a ca-

pacitative circuit through the galvanometer. In the dynamic condition

the same procedure was followed except that the mercury was with-

drawn from the cell at 10 cm/sec while discharge was occurring so

that both charge transfer effects, i.e. withdrawal of mercury from

interfacial contact with the polymer and capacitative discharge,

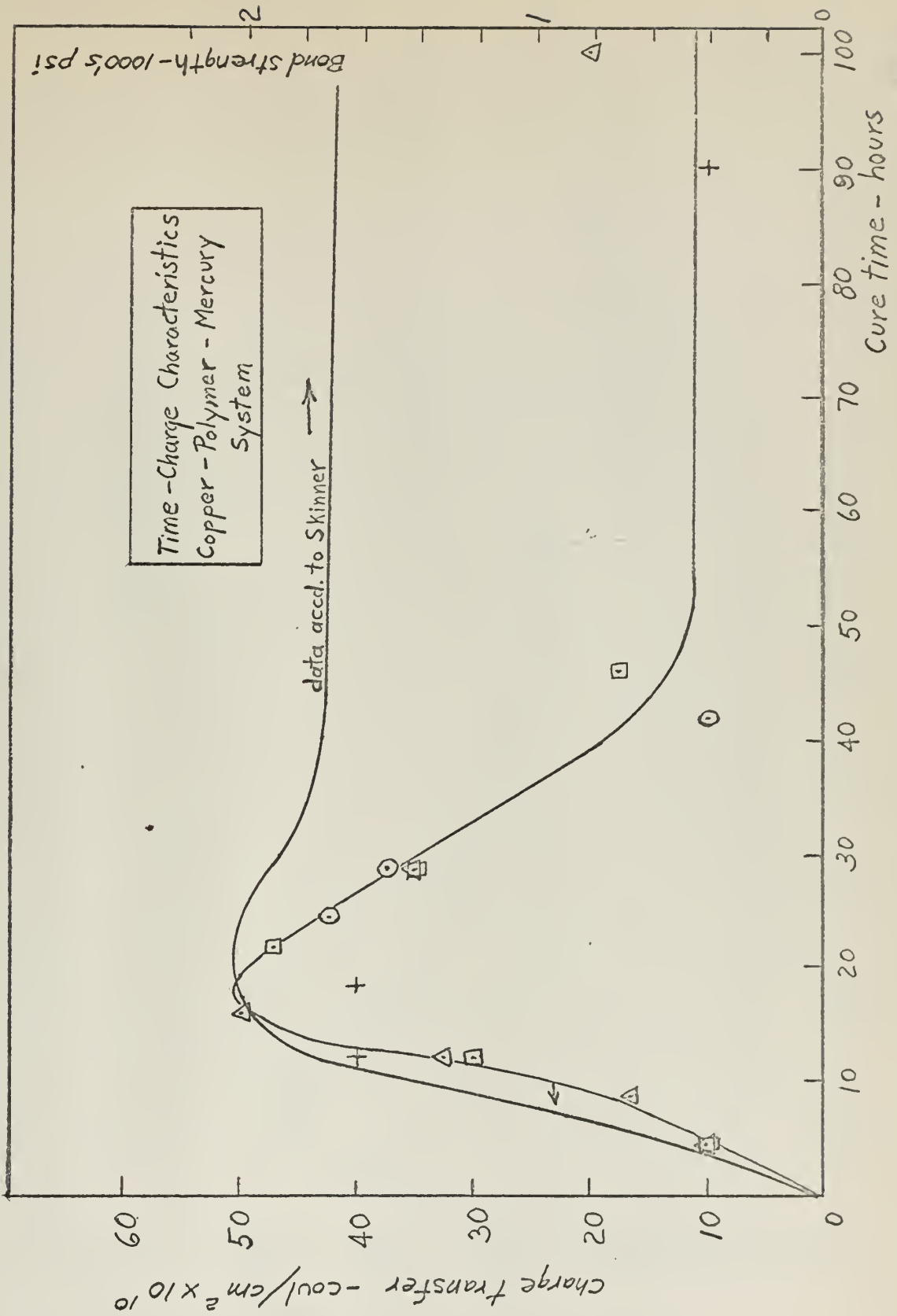could be observed simultaneously in the galvanometer deflection.
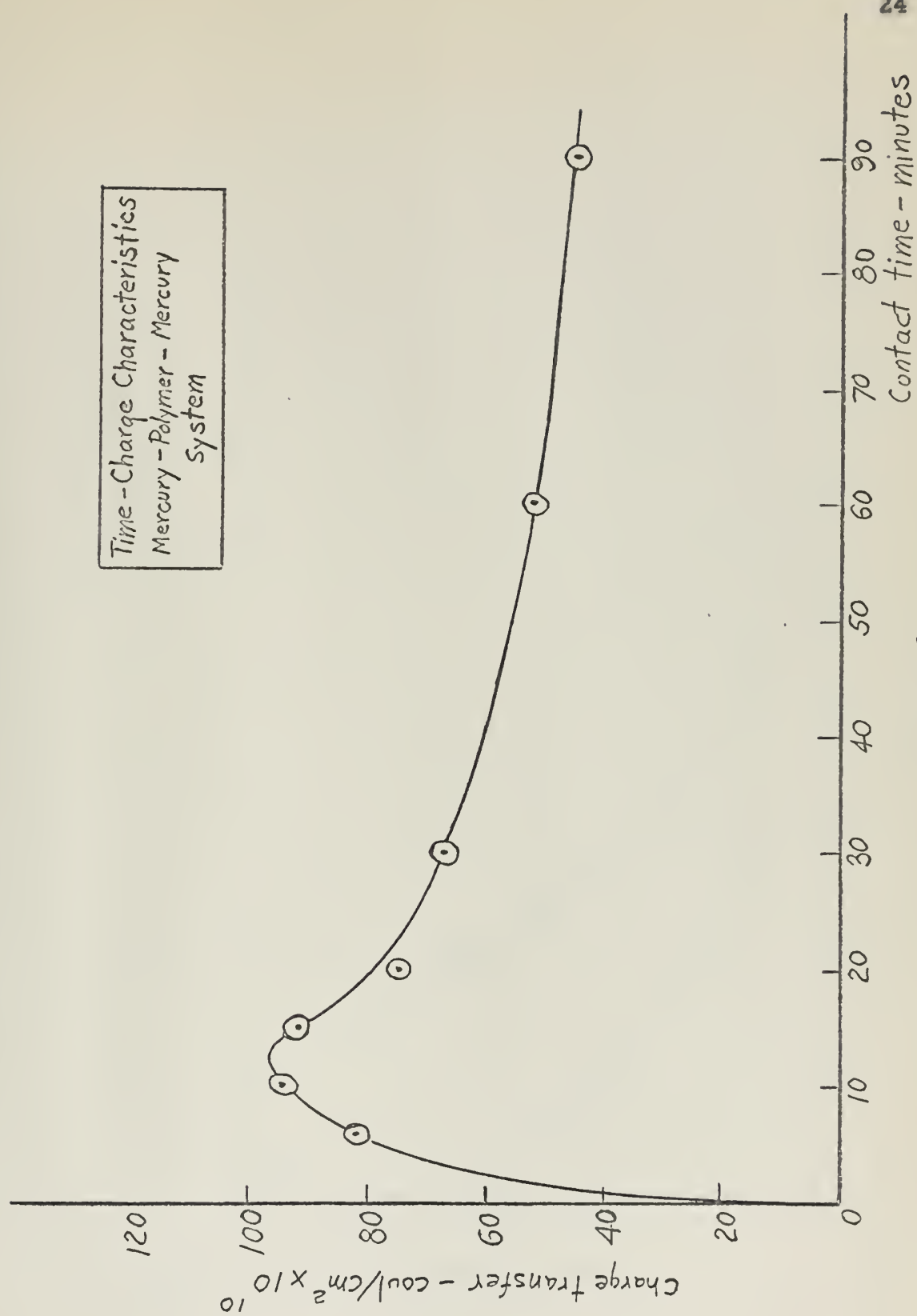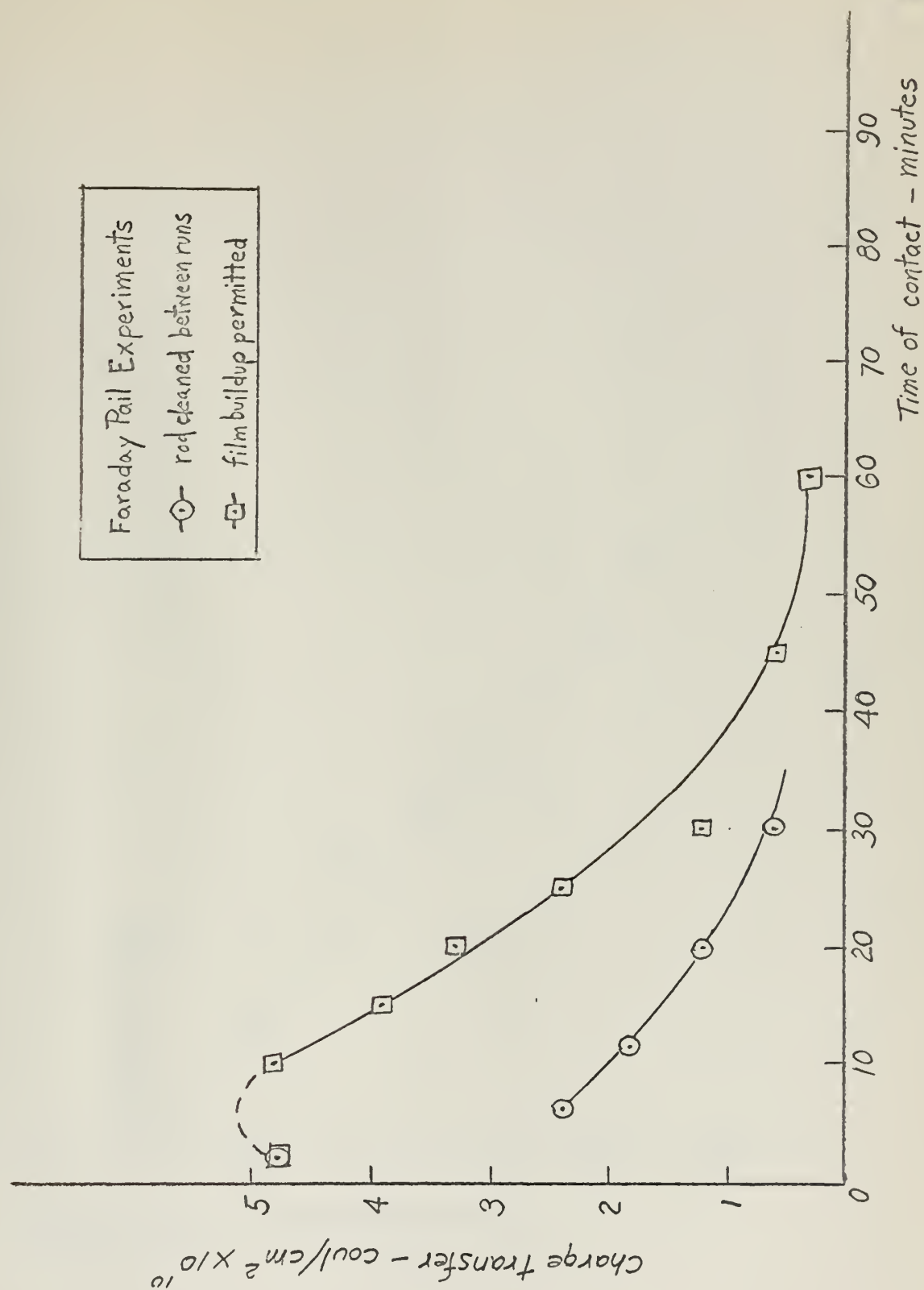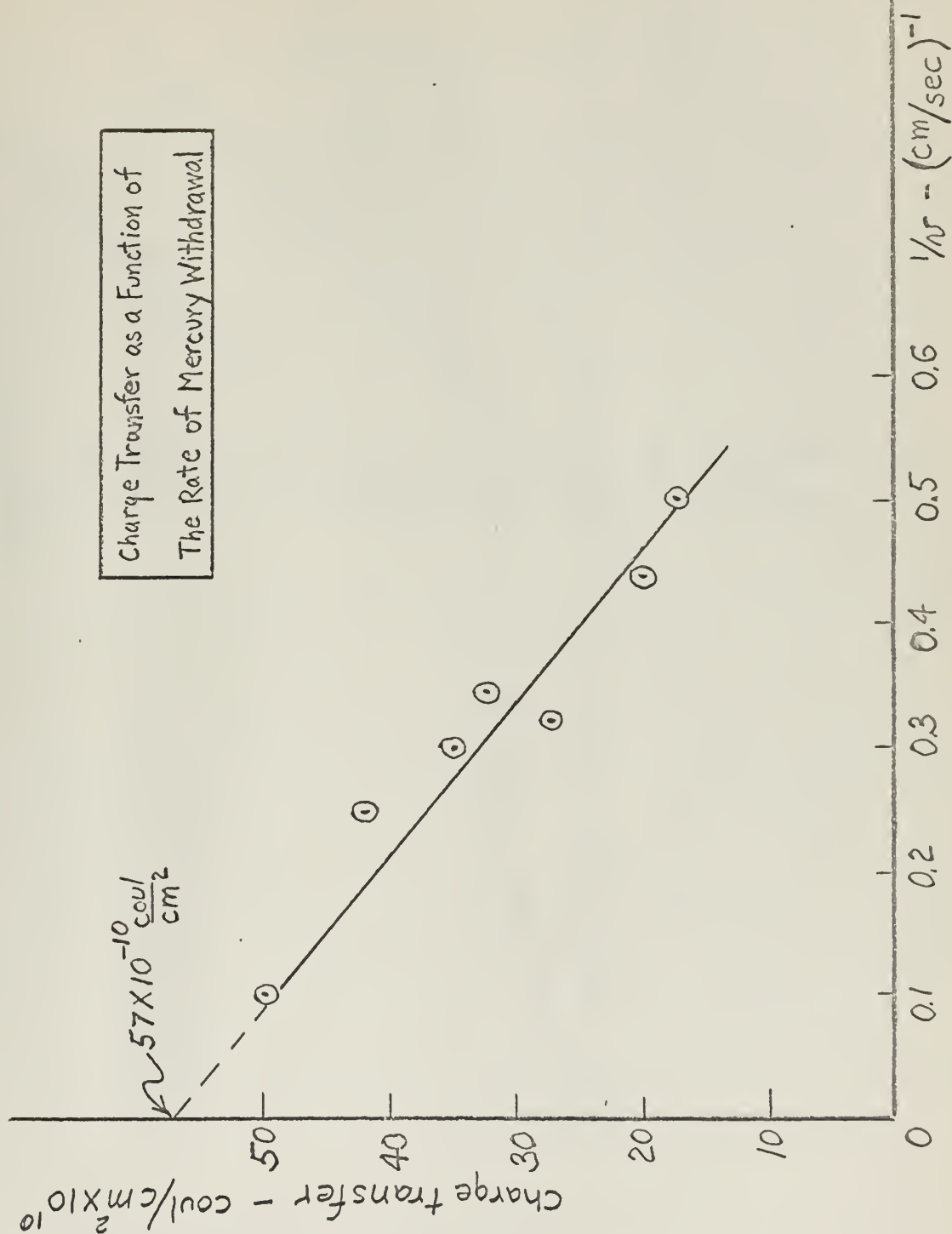
Figure 5.

Time-Charge Characteristics
Mercury-Polymer-Mercury
System

Charge transfer — coul/cm² x 10¹⁰

Contact time – minutes

Figure 6.

Faraday Pail Experiments
⊙ rod cleaned between runs
⊡ film buildup permitted

Charge transfer - coul/cm² x10¹⁰

Time of contact - minutes

Figure 7.

Figure 8.

Figure 9.

Charge Transfer as a Function of Electric Field Intensity
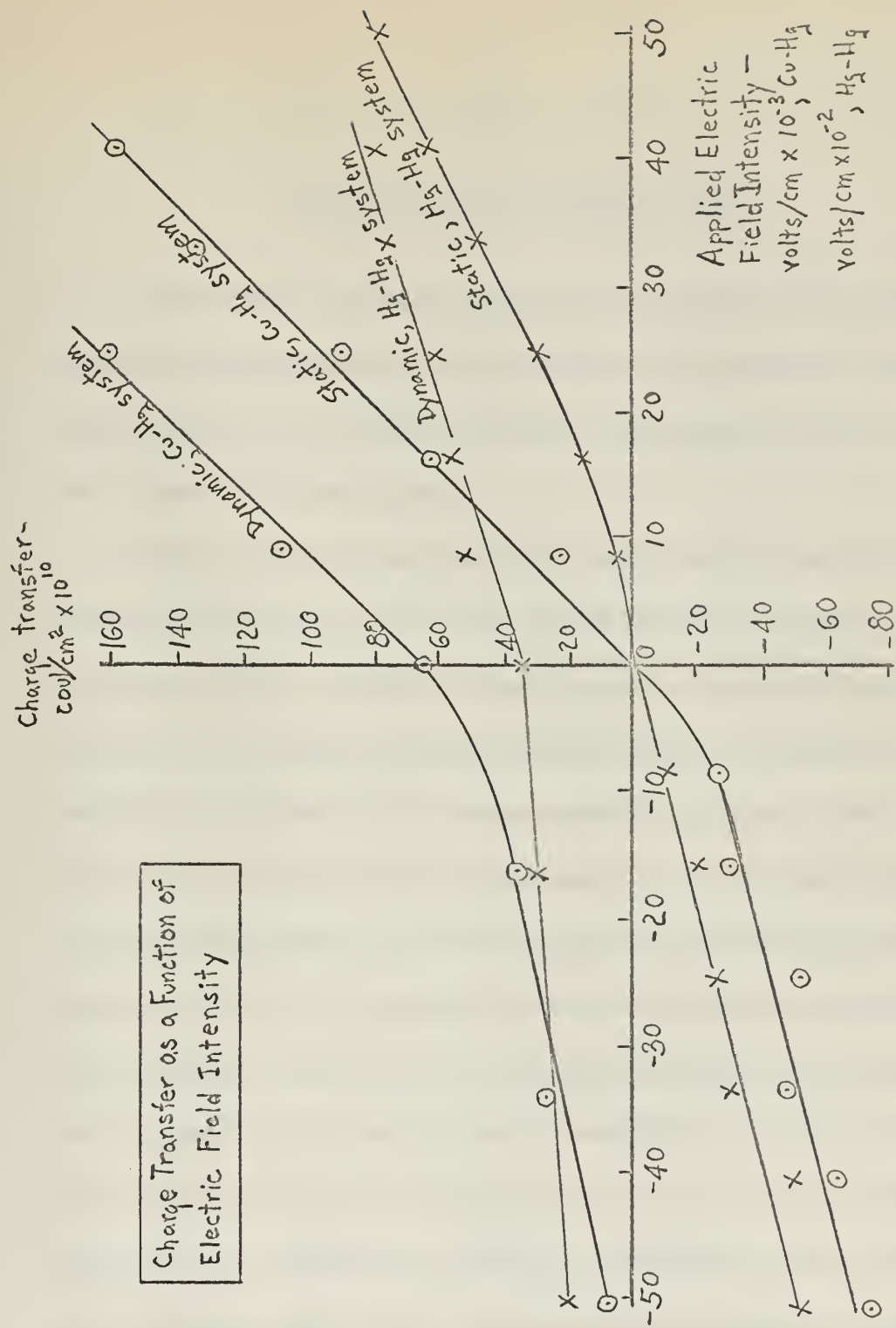
DISCUSSION AND CONCLUSIONS

The results have been reported in an order roughly corres-
ponding to the chronology in which they were obtained. At this point
the discussion will wander from this organization in order to pre-
sent a more lucid argument.

First, there are several of the experimental results which
indicate that there is some form of bulk charge distribution within
the polymer film. The time-charge transfer characteristics of
Figures 5 and 6 would indicate that some form of mobility of charge
carriers is involved in the charge transfer process. Otherwise,
one would not expect a time dependency to exist but that charge
transfer would occur immediately upon contact and thereafter remain
constant. Since we know that in the metal phase just such an electron
migration does occur and that all charge resides on the surface, we
can assume that the carriers whose mobility in this case is limiting
must reside within the bulk polymer phase and that a bulk charge
distribution at equilibrium is likely. The results of the experiments
concerning the effect of the rate of mercury withdrawal on the mag-
nitude of charge transfer summarized in Figure 8 are also germane
to this aspect of the problem.

What we are observing in these adhesion cell experiments is the charge residing in the mercury after withdrawal of the mercury from the polymer film. This charge is not necessarily the total charge transferred during the adhesion process. It is, rather, the total charge transferred less the charges which, controlled by their mobility, migrate back across the boundary during the time in which separation occurs. If the charge distribution were purely a surface distribution, charge transfer would not be velocity dependent. Since it is velocity dependent, a possible explanation is that of the existence of a bulk charge distribution.

As a side point here, it should be indicated that this velocity dependence which has also been observed in the peeling of adhesives from metal surfaces by other observers (16) was not taken into account by Deryagin in his work and that his work is therefore in error to that extent. Qualitatively, however, this does not affect his conclusions. It is seen in Figure 8 that for the copper-polymer-mercury system run under the same conditions as those used by Deryagin, the error is about 14%.

An examination of Figure 9 raises further questions regarding the electrical properties of the polymer film. It is noted that the capacitance of the polymer for the copper-polymer-mercury system is anisotropic. The capacitance in the "normal" polarity and charge transfer direction is much greater than that in the "reverse" condition.

A possible explanation for this is that mercury migration into the polymer phase may change its electrical character by adding ionic to electronic charge conduction in the polymer phase. This possibility was first raised by Skinner when he was attempting to measure the electron affinity of the polymer. Confirmation of this is obtained in the behavior of the mercury-polymer-mercury system where the capacitance in the static condition is essentially isotropic. Differences between the "normal" and "reverse" curves here are minor and might be accounted for by differences in the two surfaces of the film (the cell side was rather rough while the plug side was quite smooth) so that migration is easier in one direction than in the other. Looking at the curves for the copper-polymer-mercury system again, it is seen that the differences between the dynamic and static curves are constant and that the magnitude of charge transfer is independent of the applied electric field intensity in the range reported. This is bothersome since the mobility of charge carriers should be a function of the electric field intensity. This would lead one to the conclusion that the electric field intensity associated with the electrical double layer in the polymer phase must be very great and that Skinner's assumption that diffusion must be complete over a very shallow depth is, indeed, quite valid. It may also be observed that the range of electric field intensity used here was not great enough to bring the dynamic curve across the zero axis, an event

which one might expect to occur in the "reverse" field if the static and dynamic curves were to maintain their parallel relationships over the entire range of electric field intensity. Some anomolous behavior at extreme values of electric field intensity for the "reverse" condition was observed but these values have not been reported because of the likelihood that complicated conduction mechanisms exist under those conditions which are not relevant to the normal adhesive state.

The Faraday pail experiments, (Figure 7) although verifying the general behavior of the adhesion test cell experiments, cannot be regarded with any great quantitative reliance because the rod was so readily susceptible to electrostatic influence during cleaning and insertion and because of difficulties in achieving a reproducible rate of rod withdrawal. Some interesting qualitative observations may be made however. The production of a thin film of mercury (possibly a monolayer) over what was probably an oxide layer on the rod may be the reason for the decay of charge transfer after extended periods of contact. It is possible that as the film forms, the rod looks more and more like the bulk mercury phase so that eventually we are merely dipping a "mercury" rod in and out of a mercury well with the consequent result that charge transfer falls off to zero. The formation of such a mercury film was not noted in the adhesion test cell experiments although the oxide film was observed to develop on

the blank plugs. The probable reason for this is that the mercury
velocity was greater in the test cell and mechanical cleaning of the
plug surfaces therefore occurred. The situation may be analogous
to a surface electrophoretic effect where the original charges are
developed due to contact of the two surfaces. The appearance of an
oxide coating is also interesting. As was pointed out earlier, oxide
formation may be a significant factor in the charge transfer process
since the film defects may well be sites for local charge transfer.
Therefore, in order to achieve really definitive results a way must
be found to eliminate the formation of oxide films or to insure their
production under well controlled conditions.

Finally, some comments will be made on comparison of the
data of these experiments with the data reported by Skinner since
the original intent of this research was to make such comparisons.
It is possible from the slope of the "normal" curves of Figure 9 to
determine the dielectric constants of the polymer film and the thin
Lucite sheet.

$$C = \frac{dQ}{dV} = \frac{\epsilon K_0 A}{d} .$$

Using the parallel plate capacitor analogy for the two metal surfaces
separated by the polymer phase.

where: Q = the charge residing on the metal surface, coulombs
V = potential across the film, volts
ϵ = the dielectric constant of the polymer

K_0 = permitivity of free space, $\dfrac{\text{farads}}{\text{meter}}$

A = interfacial area, square meters
d = interfacial separation, meters
C = capacitance, farads

Thus,

$$\frac{d\,Q/_A}{d\,V/_d} = \frac{d\sigma}{d\,E} = \epsilon\,K_0$$

where: σ = surface charge density, $\dfrac{\text{coulombs}}{\text{meter}^2}$

E = electric field intensity, $\dfrac{\text{volts}}{\text{meter}}$

and

$$\epsilon = \frac{\text{slope of }\sigma\ \text{-- E curve}}{K_0}$$

For the copper-polymer-mercury system:

$$\epsilon = \frac{160 \times 10^{-10} \times 10^4}{40 \times 10^3 \times \dfrac{1}{36\pi \times 10^9} \times 100}$$

$$\epsilon = 4.5$$

For the mercury-polymer-mercury system:

$$\epsilon = \frac{75 \times 10^{-10} \times 10^4}{50 \times 10^2 \times 100 \times \dfrac{1}{36\pi \times 10^9}}$$

$$\epsilon = 17.0$$

For the "reverse" mercury-polymer-mercury system:

$$\epsilon = \frac{50 \times 10^{-10} \times 10^4}{50 \times 10^2 \times 100 \times \dfrac{1}{36\pi \times 10^9}}$$

$$\epsilon = 11.3$$

Skinner used a value of $\epsilon = 4$ in his calculations but for some reason did not experimentally determine it. The handbooks give a value of 3.6 - 3.8. It was noted earlier that the inner or plug side of the Lucite sheet making up the face of the blank plug was the smoother surface and more nearly corresponded to the type of surface on the copper plug. This and the mercury migration theory may explain why the "reverse" and "normal" dielectric constants for the mercury-polymer-mercury system are different and why the "reverse" value more closely corresponds to that of the "normal" copper-polymer-mercury system.

Using the parallel plate capacitor theory, Skinner also developed an expression converting the observed charge transfer to the equivalent mechanical force component it could produce in the adhesion system. He gives (13, p. 18):

$$\overline{f} = \frac{25.7 \, (\overline{q})^2}{\epsilon}$$

where: $\overline{f}$ = interfacial pressure due to electrostatic charge, psi

$\overline{q}$ = surface charge density, coulombs/in.^{2}

ϵ = dielectric constant of the polymer

For the copper-polymer-mercury system:

$$\bar{f} = \frac{25.7 \times (57 \times 10^{-4})^2 \times 2.54^2}{4.5}$$

$$\bar{f} = 1.2 \times 10^{-3} \, psi$$

This figure compares with a value of about 5×10^{-3} psi given by Skinner for the copper-polymer-copper system for a similar charge transfer during breaking, prepolymerization time and cure time. A similar calculation on the mercury-polymer-mercury system produces an $\bar{f} = 1.1 \times 10^{-3}$ psi even though an ϵ of 11.3 vice 4 or 4.5 was obtained here. Thus, though the systems vary greatly in nature of substrate, stripped medium and actual extents of adhesion, approximately the same electrostatic phenomena are observed in all three systems. This would lead one strongly to suspect that the electrostatic phenomena observed during the stripping of adhesive and adherend are largely mechanical in nature. However, there is still not sufficient experimental data to make a final, definitive statement concerning the origin and distribution of the observed electrical charge.

It is apparent that the electrostatic component of adhesion is very small in the case of the metal-polymer interface. The energy barrier to conduction between a metal and an insulator is so great

that in view of the magnitude of the charge transfer observed, it is
not surprising that the nature of the metal or the nature of the
contact between metal and polymer, i.e. solid-solid or solid-
liquid, should have little influence on the electrostatic effects
observed.

SUMMARY

1. A charge transfer is observed upon the separation of a mercury layer from a film of polymethylmethacrylate over a copper or mercury substrate.

2. The magnitude of the charge transfer observed in these systems is similar to that reported by Skinner for copper-polymethylmethacrylate-copper systems and is of the order of 10^{-9} coulombs per centimeter.

3. The magnitude of charge transfer is too small to contribute significantly to the total adhesive forces. If a force contribution is assigned to a separation of electrical forces at the interface, it seems to be independent of the specific nature of the metal-polymer-metal system.

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